

Effect of CaS on the electroluminescence and photoluminescence of some ZnS phosphors

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Abstract : Electroluminescent (EL) and photoluminescent (PL) spectral characteristics, voltage and frequency dependence of EL brightness are investigated for the ZnS : Cu, La, Cl phosphors after the addition of CaS. Presence of CaS increases the threshold voltage of EL emission. The acceleration-collision mechanism of EL excitation has been found to be effective for such systems. Spectral peaks and the voltage and frequency dependence of EL brightness are affected due to addition of CaS and the impurities.

Keywords : Photoluminescence, electroluminescence, CaS, ZnS phosphors

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1. Introduction

Zinc sulphide phosphors are well investigated systems [1–4]. Similarly, alkaline earth sulphides have also drawn attention of a number of workers [5–8] and are of current interest e.g. the white emitting thin film devices [9] and the multicolour emission [10]. Alkaline earth sulphides favour rocksalt structure and zinc-sulphide crystallize in zinc blende/wurtzite structure. The lattice constants of both are quite similar and the ionic radius of Ca (0.99 \AA) is not much different from that of Zn (0.74 \AA). The ionicity being 0.785 for alkaline earth sulphides and that 0.623 for zinc sulphide. Further, energy band gap of CaS is 4.41 eV and that of ZnS 3.83 eV [10]. From these data, it appears that CaS and ZnS can be mixed up and corresponding studies may prove to be interesting. Patil and Lawanger-Pawar [11] reported thermal and field excitation of filled traps in CaS : Zn phosphors by using Zn upto 2% by weight of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in their investigations. Aim of the present work is to study the effect of CaS on the PL and EL of some ZnS phosphors. Results of PL and EL spectra and voltage and frequency dependence of EL brightness under A.C. excitations are presented.

2. Experimental method

For the preparation of phosphors, a mixture of appropriate amounts of pure CaS (from National Physical Laboratory, New Delhi), ZnS (luminescent grade), copper acetate (AR, BDH), lanthanum nitrate (99.9% pure), ammonium chloride (AR, BDH) was fired at a temperature of 1050°C under the continuous flow of purified N₂ gas. The maximum impurities contained in the CaS used were Cu ≤ 20 ppm and Fe ≤ 50 ppm. The preparational method of CaS was described by Pandey and Ghosh [12–13]. CaS (without any added impurity) fired at the same temperature does not show any emission. 99.99% pure sulphur was also poured on the upper surface of above mentioned mixture. The concentrations mentioned in this paper are by weight of ZnS and represent concentrations before firing.

EL cell was prepared by pressing the powdered phosphors between a conducting glass plate and an aluminium plate to a thickness of 110 μ. An additional mica sheet of thickness 10 μ was placed above the mixture of powder sample and araldite, used as a binder. The conducting glass plate was placed above this mica sheet. The resistance of the conducting glass plate was about 200 Ω/cm². The A.C. EL excitation source was an audio oscillator (50 Hz – 20 kHz) coupled with a wide band amplifier (0 – 1 kV). The PL excitation source was 3650 Å Hg line which was obtained from a high pressure Hg lamp along with a CZ interference filter.

3. Results and discussions

3.1. EL and PL spectra

EL spectra of ZnS and CaS doped with copper and chlorine separately are shown in Figure 1. Both the spectra consist of two strong peaks with peak positions at 428 and 509 nm and 422

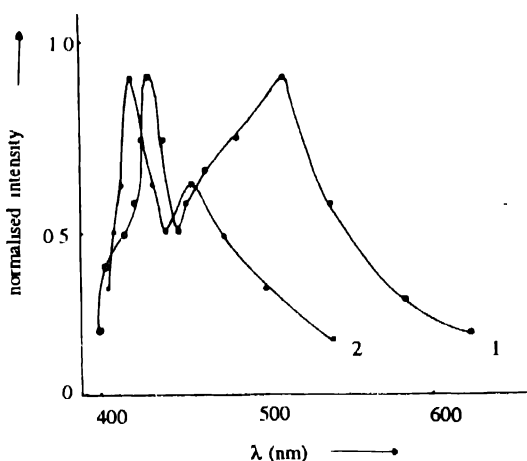


Figure 1. EL (50 Hz) Spectra of ZnS : Cu (0.01%), Cl (0.01%) (curve 1) and CaS : Cu (0.01%), Cl (0.01%) (curve 2) phosphors.

and 458 nm respectively. Effect of addition of CaS on the the EL of ZnS : Cu, Cl is shown in Figure 2. Curve no.1 shows the spectrum of combination of 90 : 10 of ZnS and CaS and

consists of three peaks at peak positions 422, 454 and 498 nm. The peaks at 422 and 454 nm are quite close to peaks of CaS : Cu, Cl at 422 and 458 nm. The third peak at 498 nm is

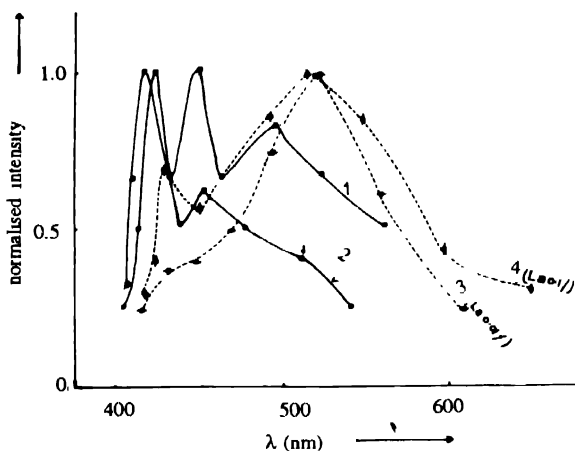


Figure 2. EL (50 Hz) Spectra of different (Zn + Ca)S phosphors ($\text{Zn}_{90} + \text{Ca}_{10}\text{S} : \text{Cu}$ (0.01%), Cl (0.01%) (curve 1); ($\text{Zn}_{80} + \text{Ca}_{20}\text{S} : \text{Cu}$ (0.01%), Cl (0.01%) (curve 2); ($\text{Zn}_{90} + \text{Ca}_{10}\text{S} : \text{Cu}$ (0.01%), La (0.01%) Cl (0.01%) --- (curve 3), ($\text{Zn}_{90} + \text{Ca}_{10}\text{S} : \text{Cu}$ (0.01%), La (0.1%) Cl (0.01%) --- (curve 4).

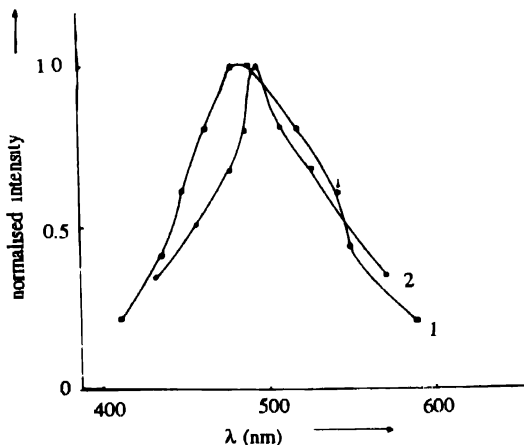


Figure 3. PL Spectra of $\text{ZnS} : \text{Cu}$ (0.01%), Cl (0.01%) (curve 1) and $\text{CaS} : \text{Cu}$ (0.01%), Cl (0.01%) (curve 2) phosphors.

similarly closer to peak at 509 nm of $\text{ZnS} : \text{Cu}$, Cl. When the concentration of CaS is increased (curve no. 2) only two peaks are seen one at 426 nm and the other at 456 nm. These peaks are represented by the centres showing the emission at 422 and 454 nm. At 80 : 20 combination of ZnS and CaS the intensity of third peak reduces and it results in a broad peak (marked by arrow) since the concentration of ZnS is comparatively lower. Curves 3 and 4 in this diagram represent the emission spectra of the systems at different concentrations *i.e.*

0.01 and 0.1% of La. The peak positions at these concentrations of La are respectively 432 and 526 nm and 432 and 520 nm. The lower peak may be due to shift of the first peak in the earlier cases and the higher wavelength peak appears to be a new peak in presence of La. The PL spectra of ZnS : Cu, Cl and CaS : Cu, Cl are shown in Figure 3. PL spectrum of former consists of a peak at about 486 nm alongwith a shoulder which can be resolved to show a broad peak on the higher wavelength side, and that of CaS : Cu, Cl consists of a peak at 490 nm. The PL spectra of systems containing different concentrations of Ca and La are shown in Figure 4. Curve No. 1 represents the spectrum at 10% CaS which consists of a strong peak

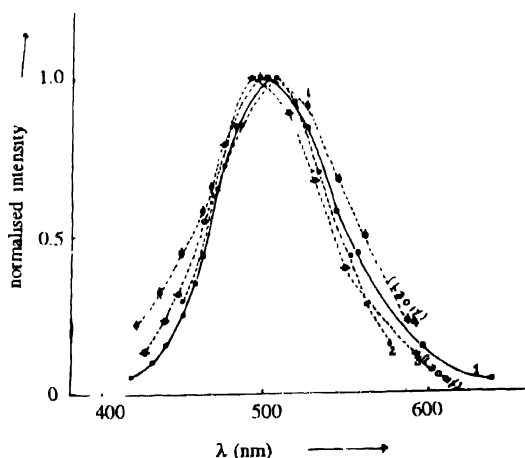


Figure 4. PL Spectra of different (Zn + Ca)S phosphors : (Zn₉₀ + Ca₁₀)S · Cu (0.01%), Cl (0.01%) (curve 1); (Zn₈₀ + Ca₂₀)S · Cu (0.01%), Cl (0.01%) ---- (curve 2), (Zn₉₀ + Ca₁₀)S · Cu (0.01%), La (0.01%), Cl (0.01%) ---- (curve 3); (Zn₉₀ + Ca₁₀)S, Cu (0.01%), La (0.1%), Cl (0.01%) ----(curve 4).

at 504 nm and that of 20% of CaS is represented by curve No. 2 in which peak at 508 nm is observed. In the case of La doped samples the spectra are represented by curves 3 and 4 and the peak positions are at 496 and 498 nm at 0.1% and 0.01% La respectively. In some of the cases shoulders (marked by arrows) are also seen.

The difference in nature of the PL and EL spectra may be due to sensitiveness of samples towards different kinds of excitations. Destriau and Ivey [14] found that spectral bands of different activators, or even two bands of the same activator may not be equally sensitive to photo and electro-excitations. One would, therefore, expect to obtain a different spectral emission depending upon the kind of excitation. For example, in ZnS : Cu exhibiting blue and green bands of Cu, these workers found the blue band to be more sensitive to electric field excitations than the green band observed in PL. Further, Bhushan *et al* [15] reported that the EL spectra of ZnO consist of more intense peaks than the PL spectra. The possibility of alloying does not seem to be possible as the emission peaks should shift towards lower wavelength side continuously on increasing the concentrations of CaS. As mentioned earlier the ionic radius of Ca being 0.99 Å and that of Zn 0.74 Å, the zinc can be

expected to be substituted in place of Ca. Ca can possibly go in the interstitials of ZnS, but this can be possible only upto an certain concentrations of Zn/Ca because beyond that concentration quenching may occur. In the present case, the concentration of Zn being quite high compared to that of Ca; it may be quite possible that upto a certain proportion, Zn is replacing Ca or Ca may go in interstitials. It is also possible that the two lattices ZnS and CaS with impurities used give rise to their own emissions. The resulting spectra may be taken as a combination of all these.

3.2. Voltage dependence :

Figure 5 shows the voltage dependence of EL brightness at different frequencies of excitations for the systems ZnS : Cu, Cl; CaS : Cu, Cl and (Zn + Ca)S : Cu, Cl. Straight lines

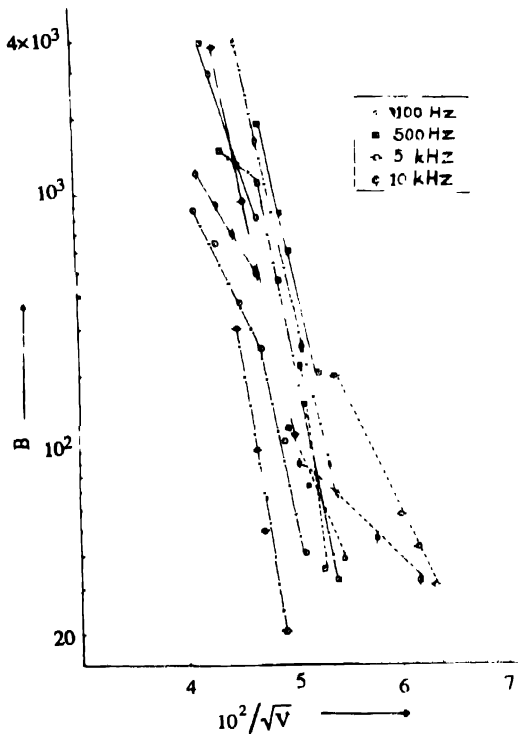


Figure 5. Voltage dependence of EL brightness for ZnS : Cu (0.01%), Cl (0.01%), ---; CaS : Cu (0.01%) Cl (0.01%) - - - - and (Zn₉₀ + Ca₁₀)S : Cu (0.01%), Cl (0.01%) — phosphors

representing the behaviour show the variation of EL brightness in all the cases according to the relation

$$B = B_0 \exp(-b/V^{1/2}), \quad (1)$$

where B_0 and b represent constants at fixed frequency of excitation and the ambient temperature. In ZnS : Cu, Cl single straight lines are obtained at different frequencies. In

CaS : Cu, Cl at lower frequencies two straight lines are observed. This shows that two modes of excitations are effective. A similar behaviour was reported by Bhushan and Chandra [8].

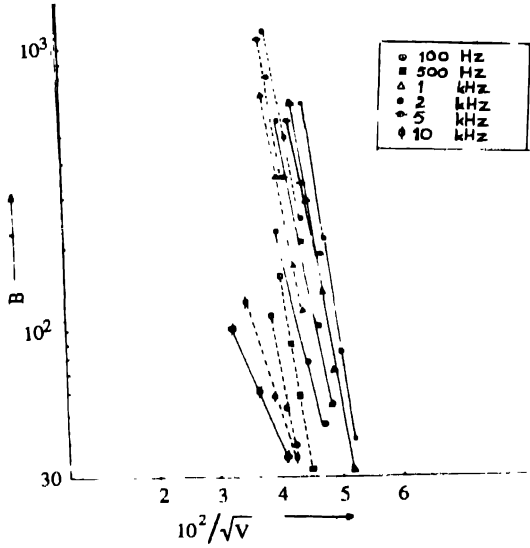


Figure 6. Voltage dependence of EL brightness for (Zn90 + Ca10) S : Cu (0.01%), La (0.01%), Cl (0.01%) - - - and (Zn90 + Ca10) S : Cu (0.01%), La (0.1%), Cl (0.01%) — phosphors.

The behaviour for (Zn + Ca)S systems is represented by a single mode of excitation. The voltage dependence of systems doped with La are shown in Figure 6. Here also only one

Table 1. The values of constants B_0 and b for different systems.

System/Freq.		100 Hz	500 KHz	1 KHz	2 KHz	5 KHz	10 KHz
ZnS : Cu, Cl	B_0	1×10^{12}	1.15×10^{10}	3×10^8	3×10^7	1.7×10^6	1×10^4
	b	391	299	235	230	137	108
CaS : Cu, Cl	B_0	4×10^{11}	5×10^{10}	2.5×10^{11}	4×10^{11}	7×10^{11}	—
	$\&$	2×10^6	4×10^4				
	b	474 & 209	547	450	445	—	—
(Zn + Ca)S : Cu, Cl	B_0	3×10^8	1.5×10^9	9×10^9	1.5×10^{11}	9×10^{10}	12×10^4
	b	405	385	436	525	587	181
(Zn + Ca)S : Cu, Cl La (0.01)	B_0	1×10^8	3×10^8	2×10^8	6×10^7	1.7×10^6	4.5×10^4
	b	350	318	195	195.6	207	—
(Zn + Ca) : Cu, Cl La (0.1)	B_0	1.6×10^{11}	3×10^8	1×10^8	1.5×10^7	4×10^6	3×10^3
	b	230	283	230	259	306	—

straight line represents the behaviour in each case. Values of constants B_0 and b derived according to the relation (1) for different systems are presented in Table 1. In ZnS : Cu, Cl B_0

and b continuously decreases with increase in the frequency. In CaS : Cu, Cl no regular behaviour is found. In (Zn + Ca)S systems doped with copper and chlorine, B_0 first increases and then finally decreases. But no regular variation is observed in b [Table 1]. In La doped systems again a similar situation is observed. Under such circumstances it is difficult to make any definite conclusion regarding the nature of these constants. It should be remembered that higher values of B can be expected for higher values of B_0 and lower values of b . This condition should hold good for efficient materials. However, the value of brightness at any voltage should be determined from the combined effect of these two constants in eq. (1). The variation according to relation (1) indicates that a barrier of Mott-Schottky type is formed [4]. At lower voltages the barrier is limited to small region and therefore the region in which EL takes place is small, but on increasing the voltage the barrier extends resulting in more light. The reason for two modes of variation may be due to the fact that after a sufficient voltage has been applied the barrier suddenly extends to larger area which together with proper conditions for acceleration of carriers results in more EL light and faster variations of brightness with further increase of voltage takes place. From the results presented in different diagrams it appears that the nature is affected by the presence of CaS and the impurities.

3.3. Frequency dependence :

The frequency dependence of EL brightness for ZnS : Cu, Cl and CaS : Cu, Cl are shown in Figure 7. The general behaviour in this figure appears to be the same *i.e.* with increase in frequency brightness first increases and after passing through a maximum at 2 kHz it starts

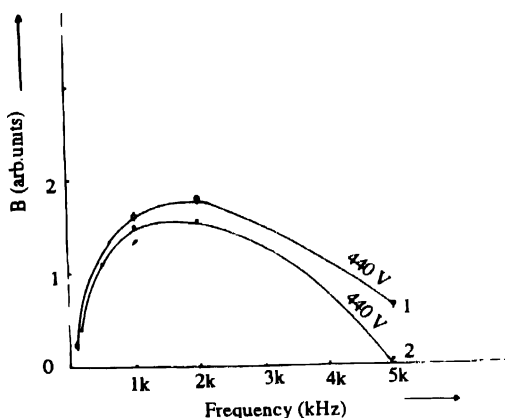


Figure 7. Frequency dependence of EL brightness at 440 V for ZnS : Cu (0.01%), Cl (0.01%) (curve 1) and CaS : Cu (0.01%), Cl (0.01%) (curve 2) phosphors

decreasing. However, the brightness at particularly higher frequencies is higher in ZnS : Cu, Cl compared to that of CaS : Cu, Cl. The frequency dependence of (ZnS + CaS) doped with copper and chlorine are shown in Figure 8. Again it is observed that the maximum appears at 2 kHz. However, the broadness of the curve is affected because of the change in the concentration of the activator Cu and Cl. The effect of La addition is shown in Figure 9. Again it is observed that the nature of the curves is affected because of its presence.

The increase in EL brightness with frequency can be understood on the basis that emptying and refilling of electroluminescent centres take place more rapidly with increase in

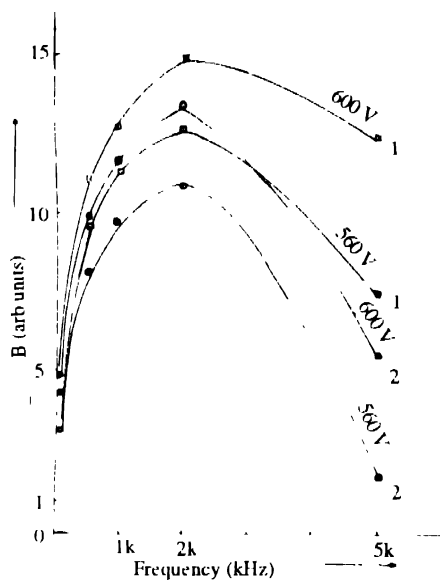


Figure 8. Frequency dependence of EL brightness for $(\text{ZnS} + \text{Ca})\text{S} : \text{Cu}, \text{Cl}$ phosphors at different concentrations of $\text{CaS} : (\text{Zn}_{90} + \text{Ca}_{10})\text{S} : \text{Cu}$ (0.01%), Cl (0.01%) (curve 1) and $(\text{Zn}_{80} + \text{Ca}_{20})\text{S} : \text{Cu}$ (0.01%), Cl (0.01%) (curve 2)

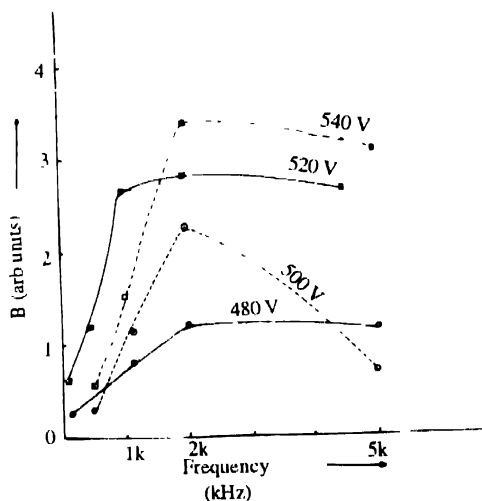


Figure 9. Frequency dependence of EL brightness for $(\text{Zn} + \text{Ca})\text{S} : \text{Cu}, \text{La}, \text{Cl}$ phosphors at different concentrations of $\text{La} : (\text{Zn}_{90} + \text{Ca}_{10})\text{S} : \text{Cu}$ (0.01%), La (0.01%), Cl (0.01%) - - - and $(\text{Zn}_{90} + \text{Ca}_{10})\text{S} : \text{Cu}$ (0.01%), La (0.1%), Cl (0.1%) —

frequency but when the time period of applied A.C. cycles becomes comparable with the lifetime of excited electrons the electron does not have enough time to emerge out from the trap. Thus the time averaged brightness will not increase linearly with frequency. The depletion of ionised activators becomes strong at higher voltages and therefore, the curves become comparatively more linear at higher voltage. The non linearity of frequency dependence at lower frequencies may also be attributed to the polarisation effect combined with the nature of depletion of ionised activator [16]. The decreasing nature of brightness for higher frequencies may be attributed to heating of the sample, and voltage losses in the transparent electrode etc [17]. It is concluded that the nature of these curves depend upon the concentration of additives like CaS and the different impurities.

4. Conclusions

Although the threshold voltage for the EL emission increases due to addition of CaS, the emission obtained at higher voltages is sufficiently good as compared to that of ZnS system. It is inferred that either zinc can be substituted in lattice of CaS or Ca can go in the interstitials of ZnS. Spectral peaks and the voltage and frequency dependence of EL brightness are affected due to presence of different additives. From voltage dependent studies the acceleration-collision mechanism is found to be effective for systems under investigation.

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